

SHOCK-INDUCED COLOR CHANGES IN NONTRONITE:  
IMPLICATIONS FOR THE MARTIAN FINESRay J. Weldon, Warren M. Thomas<sup>1</sup>, Mark B. Boslough and Thomas J. Ahrens

Seismological Laboratory, California Institute of Technology, Pasadena, California 91125

**Abstract.** Riverside nontronite, a candidate for the major mineral in the Martian fines, becomes both redder and darker upon shock loading between 180 and 300 kbar. The change from olive-yellow (2.5 Y 6/6) to strong brown (7.5 YR 4/6) in the 300-kbar sample brackets the range of color observed at the Viking lander sites. Optical microscopy, X-ray diffraction, optical, infrared, and <sup>57</sup>Fe Mössbauer spectroscopy were applied to understand the physical basis of the color change. The Riverside nontronite experienced partial dehydroxylation, probably due to shock-induced heating, that changed the coordination of the Fe<sup>3+</sup> in the octahedral layer of the clay to a mixture of 4- and 6-fold or a distorted 5-fold coordination. These changes in the clay cause the O<sup>2-</sup>-Fe<sup>3+</sup> charge transfer absorption edge to shift from the near ultraviolet into the visible, producing a redder and darker phase. The absorption spectra of both impacted and nonimpacted Riverside nontronite contains the basic features of the reflectance spectra of the bright regions of Mars: a steep drop in absorption from the near UV into the visible and a featureless near IR region. Calculations indicate that significant impact-induced color changes (and dehydration) can occur on Mars, though it seems likely that the mechanism would be more effective, volumetrically, at producing variations in color rather than affecting the absolute color.

## Introduction

Nontronite, a smectite clay with the ideal formula  $(1/2 \text{ Ca}, \text{Na})_{0.7} \text{Fe}_4(\text{Si}_{7.3}, \text{Al}_{0.7})_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , was one of a series of minerals studied to characterize the effect of impact on the chemical and mineralogical evolution of volatile-rich planetary surfaces. Nontronite, specifically, is of interest because it has been suggested to be a major mineral in the Martian fines [Toulmin et al., 1977]. Nontronite (and other minerals) do release significant amounts of water upon shock loading [Boslough et al., 1980]. Samples of Riverside nontronite, shock loaded to about 180 and 300 kbar, were found to have changed in color from yellow toward reddish brown. This paper attempts to characterize and understand the color changes and to discuss some possible implications for spectral studies of Mars.

The material used in our experiments is Riverside nontronite [Baird et al., 1977], supplied by the Viking X-Ray Fluorescence (XRF)

Team. This material was one of the best early matches for the Viking XRF spectra [Clark et al., 1977] and has been used as a base for subsequent mixing experiments to match the Martian fines [Baird et al., 1977; personal communication, 1981]. The Riverside nontronite used in our impact experiments was purified to remove as much of the nonclay phases as possible and in our samples only nontronite could be observed by optical examination, X-ray diffraction, infrared (IR), and optical spectroscopy. While no special efforts were taken to remove other clays or microcrystalline iron oxides that are common in samples like the Riverside nontronite, we feel that they were not abundant enough to alter our results substantially.

The similarity of chemistry between the two Viking lander sites [Clark et al., 1976, this issue] and the presence of global dust storms suggest that the Martian fines are homogeneously mixed on a global scale. This global mixing implies that the Martian fines contain material from a wide variety of sources and processes, so a large number of phases would be expected to be represented in the Martian fines. While it is clear that Riverside nontronite may only approximate a component of the Martian fines, we felt that a pure phase would make the impact experiments easier to interpret, and in retrospect, some of the uncertainties in our interpretations stem from the possibility of very small amounts of undetectable phases in our samples. Now that we have established that color variations within the range of those observed on Mars can be produced by impacting Riverside nontronite, other phases, including better characterized nontronites and complex mixtures more like Martian surface material, could be studied to generalize our results.

The sample preparation and shock recovery techniques used for Riverside nontronite are described by Boslough et al. [1980]. Two samples were successfully recovered after being shock loaded to peak pressures of about 180 and 300 kbar. Only several milligrams of material were recovered from the 300-kbar shot and about 0.3 g of material was recovered from the 180-kbar experiment. The samples were analyzed by optical microscopy, X-ray diffraction, optical and IR absorption spectroscopy, and <sup>57</sup>Fe Mössbauer spectroscopy. Samples of Riverside nontronite were also heated at 1 atm and compared with the impacted samples. These results and efforts made to detect magnetic minerals with a cryogenic magnetometer are summarized below. Some uncertainties exist in our results since the impact experiments were designed to characterize the loss of water, not to understand the unanticipated color changes. However, since no more experiments on nontronite are anticipated at this time, we believe that our observations warrant reporting.

<sup>1</sup>Department of Geological Sciences, University of Southern California, Los Angeles, California 90007.

The term 'nontronite' is used to denote the ideal mineral. 'Riverside nontronite' refers to the purified Viking XRF material used in our impact experiments. Other nontronite samples are named as we found them referenced in the literature or will be accompanied by the reference in which they were described. 'Martian fines' will refer to the fine-grained material actually sampled by the Viking landers, and 'Martian surface material' will be used as a more general term for material existing on the Martian surface.

### Experimental Results

#### Color Change: Yellow to Reddish Brown

The Riverside nontronite used in the impact experiments is olive-yellow (2.5 Y 6/6) in the Munsell soil color terminology [Munsell, 1975]. The sample shocked to 180 kbar shows only a very slight color change, toward yellowish brown (1.0 Y 5/6). The sample shocked to 300 kbar shows a marked color change to strong brown (7.5 YR 4/6). Both samples show a shift in hue toward red and value toward black. The higher-pressure impact caused the material to become both redder and darker.

Upon microscopic examination, the material appeared essentially unchanged except for color. However, the fine grain size and poor optical character of the clay precluded detailed characterization of the optical properties of the samples so we cannot determine if they have been affected. Particles of stainless steel (68% Fe, 19% Cr, and 10% Ni) from the sample holder were blackened and appeared altered, suggesting chemical interaction with the samples. Sample stuck to pieces of steel were not obviously different from pieces of sample that were free of steel, so we concluded that the change in the steel was largely caused by hot water vapor released during the shock event. Future experiments should probably use a less reactive sample holder, especially one that does not contain iron.

The optical and near IR absorption spectrum (Figure 1) for our Riverside nontronite sample is very similar to published optical absorption spectra of nontronite. Karickhoff and Bailey [1973, pp. 62-63] assign the very strong absorption bands in the near ultraviolet (UV) to  $O_2^-$ - $Fe^{3+}$  charge transfer. The absorption due to these broad bands decreases rapidly from the near UV into the visible. Four shoulders on the visible edge of the charge transfer bands appear between 367 and 520 nm and are assigned by Karickhoff and Bailey [1973] to crystal field transitions in  $Fe^{3+}$ . Slope changes and shoulders in the Riverside nontronite in this region may be the result of these transitions. There is no evidence for  $Fe^{2+}$ , which would have strong crystal field absorptions near 1000 nm, and the spectra are quite featureless in the near IR.

The sample shocked to 180 kbar has virtually the same optical and near-IR absorption spectrum as the unimpacted sample. This is consistent with the slight color change. In the Riverside nontronite shocked to 300 kbar, the very strong absorption centered in the UV extends further into the visible, absorbing a substantial amount of the blue end of the visible spectrum (see Figure 1).

This is consistent with the redder and darker color observed in the impacted samples. Slope changes and the minor structure attributed to crystal field effects are also obscured.

#### X-Ray Diffraction and IR Spectroscopy: Water Loss

The major changes observed in the X-ray diffraction and IR absorption spectra can be explained by the loss of water and disordering associated with the shock events [Boslough et al., 1980]. Some of the discussion from Boslough et al. [1980] is repeated here since it bears on the structural changes associated with the color change. Riverside nontronite has a very strong X-ray diffraction peak at 14.9 Å, moderately strong peaks at 4.51 and 1.51 Å and small peaks near 3.5 and 2.6 Å. All of these peaks are typical of nontronite [Berry, 1974]. After impact, the width of the structural layers decreased, with  $d = 11.7$  Å for the product of the 300-kbar shot. The other peaks remained essentially unchanged, and no obvious new peaks appeared. The decrease in the dimension of the structural layers is consistent with a loss of about 2/3 of the interlayer water [Boslough et al., 1980]. The amount of interlayer water, however, is highly dependent upon sample preparation and handling so this value must be considered tentative.

The IR absorption spectra of Riverside nontronite also indicates dehydration [Boslough et al., 1980]. Figure 2 shows the detail of the water-stretching region for Riverside nontronite and Riverside nontronite impacted to 300 kbar.

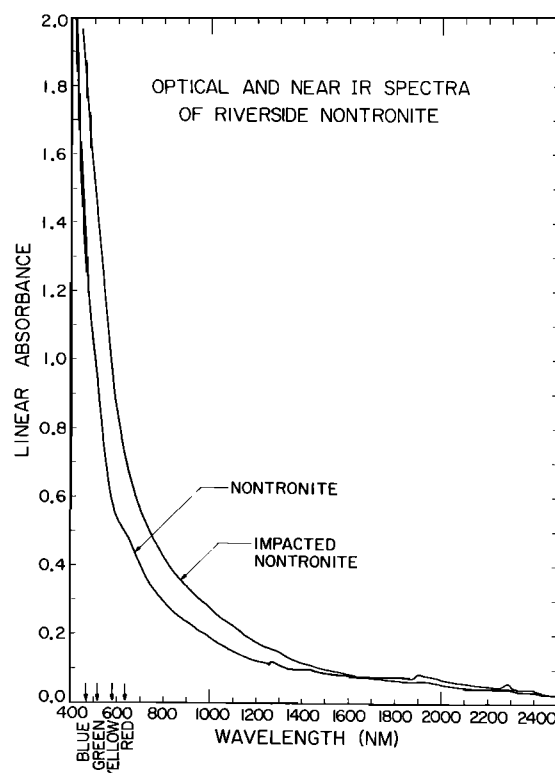


Fig. 1. Optical and near-infrared (IR) spectra of Riverside nontronite and Riverside nontronite shocked to 300 kbar.

The large drop in intensity of both the structural ( $\sim 3550\text{ cm}^{-1}$ ) and interlayer ( $\sim 3400\text{ cm}^{-1}$ ) water suggests substantial water loss on impact. The decrease in structural water is greater than interlayer water. This seems contrary to dehydration studies on clays, which suggest that most of the interlayer water is lost before substantial structural water is removed [MacKenzie and Rogers, 1977]. We infer that more interlayer than structural water was actually removed during the impact event but that substantial interlayer water was reabsorbed immediately after the event or sometime before the IR spectra could be generated. Reabsorption of the structural water was inhibited by kinetic boundaries [Boslough et al., 1980].

In the 180-kbar shot about 3 wt % vapor was directly detected [Boslough et al., 1980, p. 2152]. However, no significant water loss could be documented by IR absorption. This could be explained if most of the water loss was interlayer water that was replaced by the time the IR spectra was taken. In summary, both samples lost interlayer water upon impact though an undetermined amount returned after the event. The 180-kbar sample probably lost very little structural water and the 300-kbar sample showed a significant and irreversible loss of structural water. Since the 300-kbar sample also showed a marked color change and the 180-kbar sample was

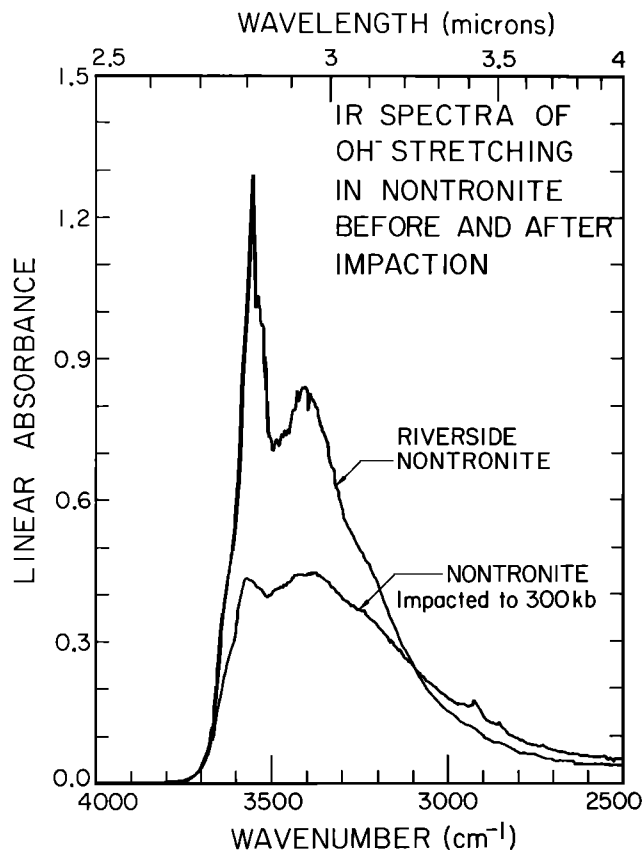


Fig. 2. IR spectra of Riverside nontronite and Riverside nontronite shocked to 300 kbar. The sharp peaks near  $3550\text{ cm}^{-1}$  are due to structurally bound hydroxyl water ( $\text{OH}^-$ ) and the broad peaks near  $3400\text{ cm}^{-1}$  are interlayer molecular water.

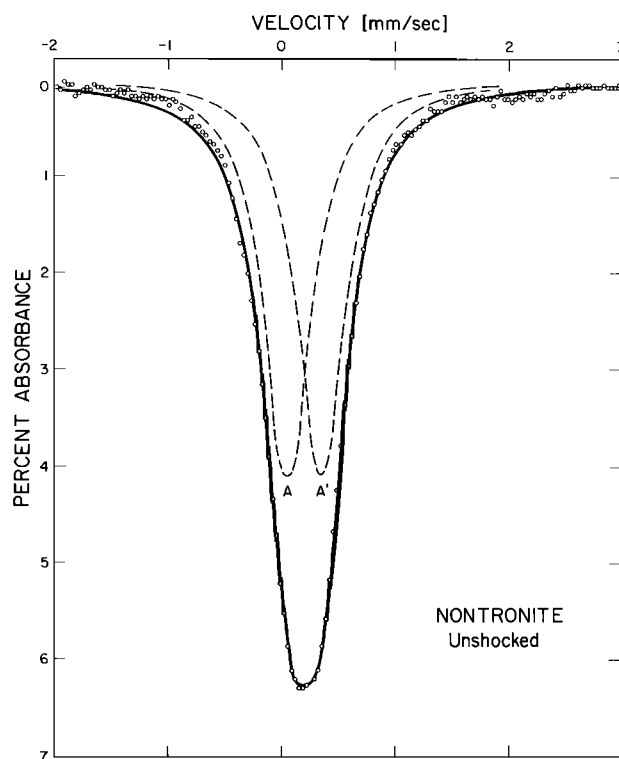


Fig. 3. The  $^{57}\text{Fe}$  Mössbauer spectrum of Riverside nontronite.

only slightly changed in color, the dehydroxylation seems directly related to the color change.

Many workers have attributed subtle peaks and position changes in both the X-ray diffraction pattern and IR absorption spectra to the presence of particular cation siting in nontronite [e.g., Goodman et al., 1976; Russell and Clark, 1978]. Our data are not of sufficient quality to infer the site distribution of the iron that might help explain the color change. However, inferences about the cation siting will be made from the Mössbauer spectroscopy and structural arguments based on the documented dehydroxylation.

#### Mössbauer Spectroscopy: The $\text{Fe}^{3+}$ Environment

Since the optical spectra of unshocked and shocked Riverside nontronite are dominated by ferric iron and the color changes may be controlled by some change in the environment of the  $\text{Fe}^{3+}$  cation,  $^{57}\text{Fe}$  Mössbauer spectra were collected on the samples to determine the environment of the iron. From the isomer shift of the peak for Riverside nontronite (Figure 3, Table 1) it is evident that the sample contains  $\text{Fe}^{3+}$ , dominantly in octahedral coordination [Bancroft, 1973]. Two different samples of Riverside nontronite were run to test the homogeneity of the starting material and were found to be virtually identical (see Table 1). The spectrum is adequately fit with a single  $\text{Fe}^{3+}$  doublet, as shown (Figure 3). The rather broad line width ( $0.53\text{ mm/s}$ ) suggests the presence of a number of almost completely overlapped, unresolvable doublets that on the average match the parameters indicated. This is likely to mean that the  $\text{Fe}^{3+}$

TABLE 1. Hyperfine Parameters for  $^{57}\text{Fe}$  Mössbauer Spectra of Nontronites

Sample	Site	Percent Area	Isomer Shift	Quadrupole Splitting	Line Width	Percent Misfit
Riverside nontronite (Figure 3)	$\text{Fe}^{+3,\text{VI}}$	100	0.19	0.30	0.53	0.109
Riverside nontronite	$\text{Fe}^{+3,\text{VI}}$	100	0.19	0.30	0.57	0.211
Riverside nontronite impacted to 180 kbar (Figure 4)	$\text{Fe}^{+3,\text{VI}}$	51.7	0.20	0.28	0.61	0.099
	$\text{Fe}^{+3,\text{VI}}$	48.3	0.21	0.99	0.61	
Riverside nontronite impacted to 300 kbar (Figure 5a)	$\text{Fe}^{+3,\text{V-VI}}$	100	0.15	0.37	0.65	0.398
Riverside nontronite impacted to 300 kbar (Figure 5b)	$\text{Fe}^{+3,\text{VI}}$	62.2	0.19	0.37	0.51	0.327
	$\text{Fe}^{+3,\text{IV}}$	37.8	-0.01	0.46	0.51	
Riverside nontronite heated to 350°C (Figure 6)	$\text{Fe}^{+3,\text{V-VI}}$	100	0.16	0.27	0.56	0.211
Riverside nontronite heated to 500°C (Figure 7)	$\text{Fe}^{+3,\text{V-VI}}$	100	0.18	1.00	0.68	0.317
Nontronite <sup>a</sup> Goodman et al. [1976]	$\text{Fe}^{+3,\text{VI}}_{\text{cis}}$	44-70	0.17-0.20	0.25-0.34	0.32-0.38 <sup>b</sup>	c
	$\text{Fe}^{+3,\text{VI}}_{\text{trans}}$	19-48	0.15-0.21	0.60-0.67	0.25-0.41 <sup>b</sup>	
	$\text{Fe}^{+3,\text{IV}}$	0-32	-0.01-0.01	0.47-0.61	0.22-0.35 <sup>b</sup>	

All values are in mm/s. Isomer shift is relative to Fe in palladium at room temperature.

<sup>a</sup>Originally measured relative to metallic Fe at 77°K; we converted them to our standards by subtracting 0.185 mm/s. to correct from metallic Fe to Fe in Pd, and by subtracting 0.110 mm/s. to correct from 77°K to room temperature.

<sup>b</sup>Narrow peaks reflect three doublets (whereas ours are 1 or 2) and better samples.

<sup>c</sup>Goodman et al. [1976] used  $\chi^2$  or a 'goodness of fit' which is not directly comparable to our misfit.

site is somewhat variable. The fact that the fit slightly underestimates the data in the region between 2 and 2.5 mm/s may indicate the presence of a very small amount of  $\text{Fe}^{2+}$  [Bancroft, 1973]. However, as also indicated by the optical spectra, the  $\text{Fe}^{2+}$  can at most represent several percent of the iron in the samples.

The Mössbauer spectra of the Riverside nontronite shock loaded to 180 kbar has changed considerably (Figure 4). The data are best fit by two sets of octahedral doublets, with the hyperfine parameters listed in Table 1. The major component (A-A' in Figure 4) is essentially the same as the  $\text{Fe}^{3+}$  site in the unshocked material. The minor component (B-B' in Figure 4) has an isomer shift indicating octahedral  $\text{Fe}^{3+}$ , but the quadrupole splitting has become much larger: 0.99 mm/s. The fact that the data are fit by assuming two  $\text{Fe}^{3+}$  sites does not necessarily require well-defined sites; there could be a large amount of variation in actual distortion that is approximated, on average, by the two doublets that fit the data. The moderately broad line widths (0.61 mm/s) suggest this possibility.

The Riverside nontronite sample shocked to 300 kbar (Figure 5) is unlike either the starting material or the 180 kbar sample. The data can be fit with one (Figure 5a) or two (Figure 5b)

doublets with the hyperfine parameters listed on Table 1. Statistically, the improvement in misfit achieved by using two doublets (Figure 5b) instead of one (Figure 5a) is probably not significant. This is surprising since Figure 5b 'looks' better than Figure 5a in that it approximates the asymmetric shape of the data. The high misfit value for the 300-kbar sample appears to be due primarily to the poor quality of the data resulting from the very small sample size. Comparing Figure 5 with Figures 3 and 4 shows that the data are intrinsically more scattered for the 300-kbar sample. The low sample density is also reflected in the low absorbance of the 300-kbar sample. Besides the marginal improvement in misfit, the improvement in line width, 0.51 mm/s versus 0.68 mm/s, and the actual isomer shift of the peaks may argue for the two component fit (Figure 5b). The isomer shifts, 0.19 mm/s for A-A' and -0.01 mm/s for B-B' are characteristic of octahedral and tetrahedral sites, respectively, in silicates. See Table 1 for the reported values in nontronite from Goodman et al. [1976]. While this could simply be a coincidence, combined with the observations above it lends credence to preferring the two-component fit. The isomer shift of 0.15 mm/s for the one-component fit is too low to be an octahedral site and too high to

be a tetrahedral site. It may represent a hybrid site between 6- and 4-fold coordination. The implications of these two possibilities will be discussed below.

#### Heating Experiments: Thermal Decomposition of Nontronite

Samples of Riverside nontronite were heated to temperatures up to 550°C for half hour intervals in an attempt to match the results of the impact experiments with heated samples. Samples heated in air achieved approximately the same color as the 180- and 300-kbar samples at about 300°C and 500°C, respectively. Samples heated in a reducing environment became darker much faster than they became redder and could not match the impacted samples. This may suggest that if the change was due to only heating, the environment may be important. Mössbauer spectra of samples heated to 350°C and 500°C were taken to compare with the impacted samples.

The sample heated to 350°C (Figure 6) is quite similar to the sample impacted to 300 kbar in isomer shift but is quite different from the 180-kbar sample. The sample heated to 350°C has a small drop in isomer shift and, possibly, a smaller quadrupole splitting (Table 1). The sample heated to 500°C (Figure 7, Table 1) is unlike either the original Riverside nontronite or either impacted sample. The fit (Figure 7) is poor, but since the spectrum is so unlike the impacted samples, little effort was expended to identify its minor components.

#### Discussion

##### The Fe<sup>3+</sup> Siting in Riverside Nontronite

There is some controversy about the siting of the Fe<sup>3+</sup> in nontronites. Ideally, there are three

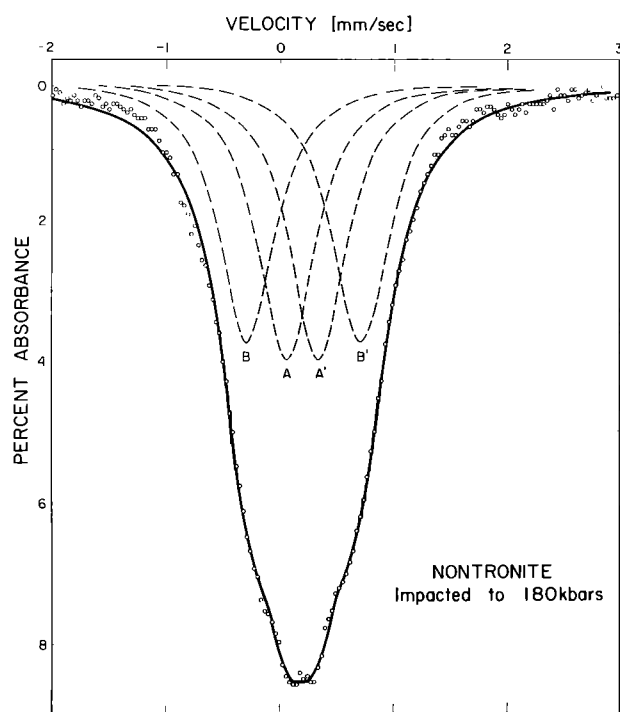


Fig. 4. The <sup>57</sup>Fe Mössbauer spectrum of Riverside nontronite shocked to 180 kbar.

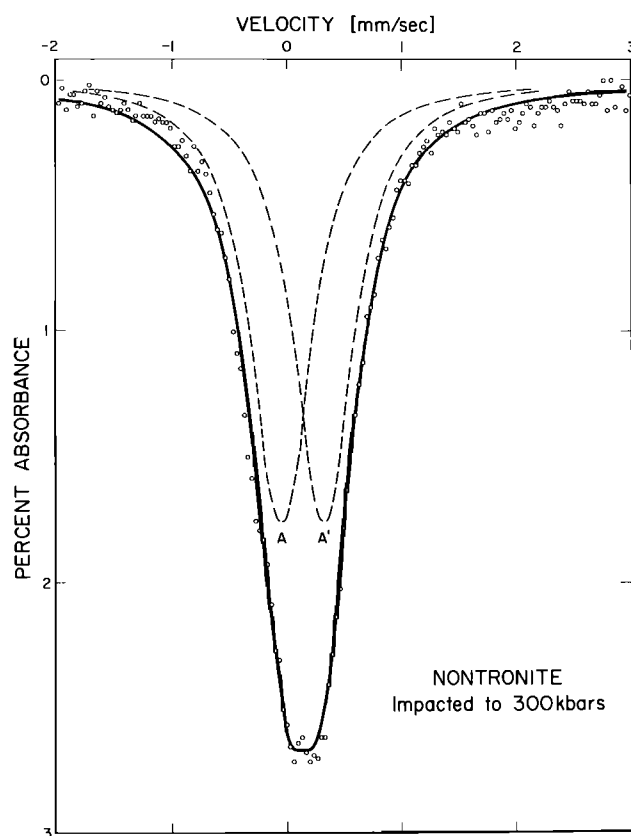


Fig. 5a. The <sup>57</sup>Fe Mössbauer spectrum of Riverside nontronite shocked to 300 kbar.

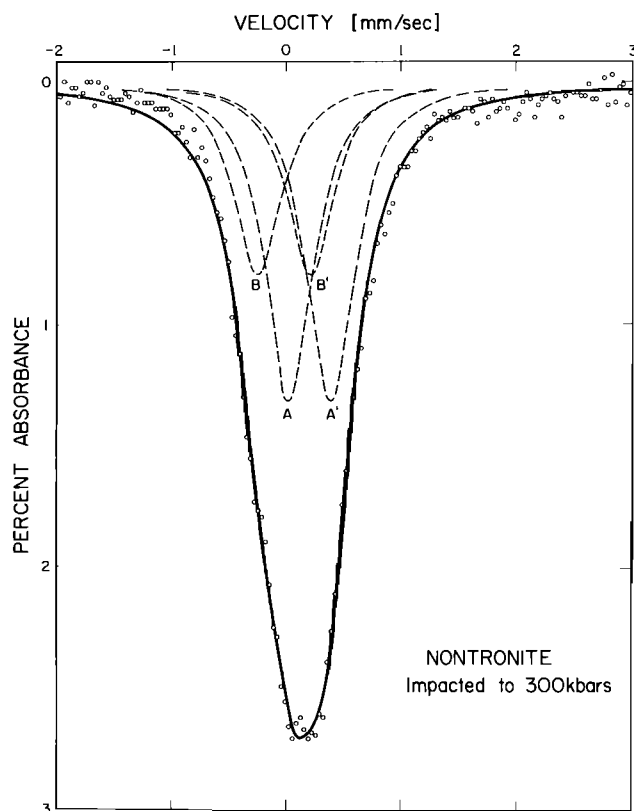


Fig. 5b. The <sup>57</sup>Fe Mössbauer spectrum of Riverside nontronite shocked to 300 kbar.

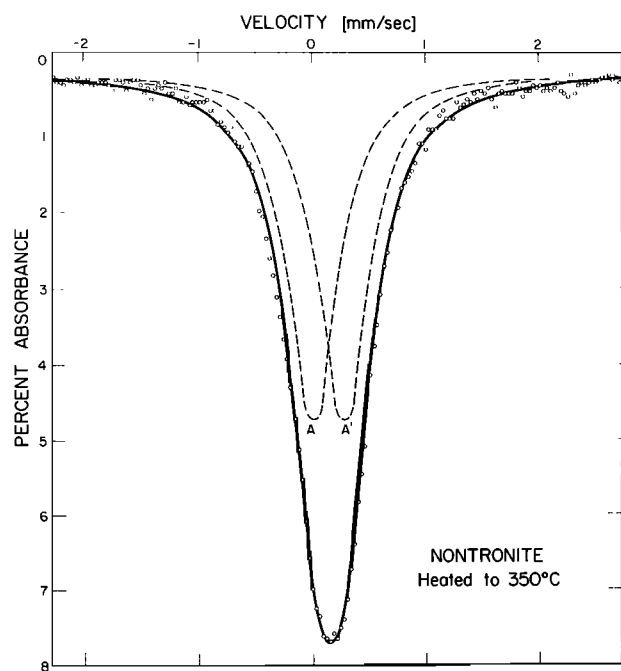


Fig. 6. The  $^{57}\text{Fe}$  Mössbauer spectrum of Riverside nontronite heated to  $350^\circ\text{C}$ .

general sites for the  $\text{Fe}^{3+}$ : an octahedral site with a *cis* configuration of the  $\text{OH}^-$ , an octahedral site with a *trans* configuration of the  $\text{OH}^-$  and a tetrahedral site [Goodman et al., 1976]. More  $\text{Fe}^{3+}$  environments are possible by distorting a portion of one of these sites or by differences in the nearest neighbor cations [Goodman, 1978]. Goodman et al. [1976] found three sites occupied in almost every nontronite they studied, with the *cis* octahedral site always dominating. The range of values for the hyperfine parameters determined from the Mössbauer spectra are included for comparison in Table 1. Brunot [1973] found the same three sites. Rozenson and Heller-Kallai [1977] and Heller-Kallai and Rozenson [1980] only report  $\text{Fe}^{3+}$  in octahedral sites, again with the *cis* configuration dominating. Goodman [1978] points out that a sample of nontronite inferred to have only *cis* octahedral  $\text{Fe}^{3+}$  using electron diffraction [Mering and Oberlin, 1967] had what had been interpreted as both *cis* and *trans* octahedral  $\text{Fe}^{3+}$  from his Mössbauer studies. From this he speculates that what had been inferred to be a *trans* configuration may actually be a distorted *cis* configuration, possibly due to the presence of tetrahedral  $\text{Fe}^{3+}$  in adjacent sites.

Fortunately, the present Mössbauer spectra only show one resolvable  $\text{Fe}^{3+}$  doublet that matches the *cis* octahedral site that all authors agree on. A nontronite reported by Taylor et al. [1968] is similar to ours in its single doublet fit. As shown in Table 1, our isomer shift of  $0.19 \text{ mm/s}$  is within the range of  $0.17$  to  $0.20 \text{ mm/s}$  found by Goodman et al. [1976] in a study of seven nontronites. The present quadrupole splitting of  $0.30 \text{ mm/s}$  is also within the range of  $0.25$ – $0.34 \text{ mm/s}$  reported by Goodman et al. [1976]. This is in contrast to their *trans* site that has quadrupole splittings between  $0.60$  and  $0.67 \text{ mm/s}$ . The fit can be improved slightly (misfit of  $0.080\%$

versus  $0.109\%$ ) by adding up to  $5\%$  tetrahedral  $\text{Fe}^{3+}$  with the parameters given by Goodman et al. [1976] (see Table 1). However, since an unconstrained fit including tetrahedral  $\text{Fe}^{3+}$  could not resolve this peak, we cannot infer that there is really any tetrahedral  $\text{Fe}^{3+}$  in the starting material.

These Mössbauer spectra for Riverside nontronite are consistent with previously reported ferric nontronites. However, the data do not eliminate the possibility of small amounts of certain iron oxides, since it would be difficult to resolve small amounts of iron oxides or hydroxides with  $\text{Fe}^{3+}$  environments similar to those in nontronite. We can, however, rule out significant amounts of magnetic minerals like maghemite, hematite, or goethite, unless they occur in crystallites small enough to be superparamagnetic, because of the lack of the highly distinctive six-line magnetic signature in our spectra [Bancroft, 1973; Sprenkel-Segel, 1970].

The  $180\text{-kbar}$  sample is distinguished by a new component characterized by a large quadrupole splitting. The most likely possibility for this change is that many of the  $\text{Fe}^{3+}$  sites were simply distorted in the shock event. Increasing distortion of the coordination sphere of the iron typically leads to larger quadrupole splitting [Bancroft, 1973]. Another possibility is that B-B' is not a nontronite site at all. Microcrystalline ferric oxides, hydroxides, and gels have quadrupole splitting for  $\text{Fe}^{3+}$  octahedral sites up to  $1.20 \text{ mm/s}$  [Goodman et al., 1976, p. 56]. This possibility seems unlikely because it would require major changes in the Riverside nontronite that is not observed by either X-ray diffraction or IR spectroscopy.

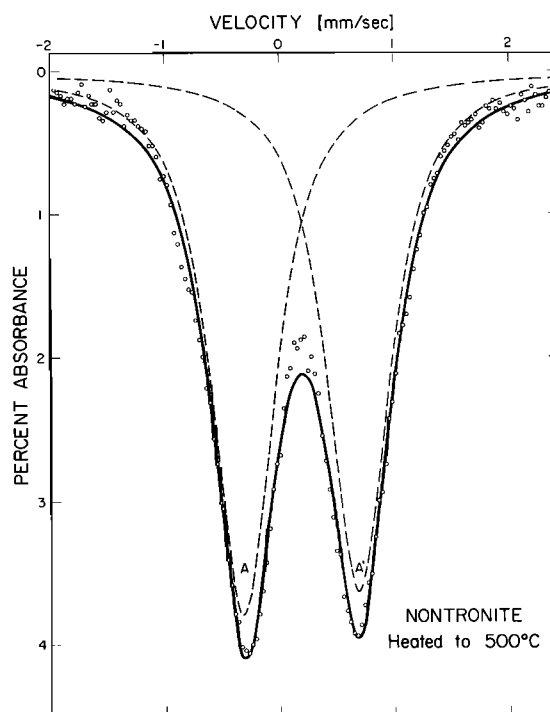


Fig. 7. The  $^{57}\text{Fe}$  Mössbauer spectrum of Riverside nontronite heated to  $500^\circ\text{C}$ .

As with the 180-kbar sample, we have interpreted the 300-kbar sample by analogy with unimpacted nontronite. Again, this is because the X-ray and IR data suggest that the sample is still basically nontronite, though dehydrated and reddened. If the sample impacted to 300 kbar has new phases in it, they should be characterized by tetrahedral  $\text{Fe}^{3+}$ , or at least a lower coordination number than 6, since that is the component not present in the starting material. The only possible minerals that have tetrahedral  $\text{Fe}^{3+}$ , leading to such low isomer shifts, are maghemite and lepidocrocite [Armstrong et al., 1966; Greenwood and Gibb, 1971; Sprenkel-Segel, 1970]. If maghemite is present it must be in crystallites smaller than 200 Å so that it is superparamagnetic, since we have a two-line spectrum and not the magnetic six-line signature [Coey, 1971; Berkowitz et al., 1968]. Also, if the tetrahedral  $\text{Fe}^{3+}$  is exclusively in maghemite or lepidocrocite, the size of the doublet would require that about 1/3 of the material shocked to 300 kbar be iron oxide. Mixing experiments suggest that more than a few percent of maghemite would make the Riverside nontronite far redder than the 300-kbar sample. These observations, coupled with the X-ray and IR results, demand that most or all of the tetrahedral  $\text{Fe}^{3+}$  be part of the clay.

By comparing the heating history of Riverside nontronite with our impacted samples we can infer how the iron site changes with shock heating. Published heating data on nontronite show that the changes take place continuously within the clay structure until the nontronite dissociates into oxides at 600°C to 800°C [MacKenzie and Rogers, 1977; Heller-Kallai and Rozenson, 1980]. Heller-Kallai and Rozenson's [1980] nontronite starts with both *cis* and *trans* octahedral sites. As heating progresses and dehydroxylation occurs, the *cis* site converts toward a 5-fold coordination while the *trans* site remains 6-fold. Both sites' quadrupole splitting increases dramatically after about 400°C. Upon heating above 600°C the sample decomposed and a six-line magnetic spectrum characteristic of hematite appeared.

Riverside nontronite follows a similar path except that there is only the *cis*  $\text{Fe}^{3+}$  site to follow. The decrease in isomer shift in the 350°C sample is appropriate for a shift from 6-fold toward 5-fold coordination. The slight decrease in quadrupole splitting is difficult to explain, but other nontronites do not show a great increase in quadrupole splitting until higher temperatures so this may not be significant. Our 500°C sample very closely matches the *cis* component in the nontronite heated to 500°C by Heller-Kallai and Rozenson [1980]. It also resembles MacKenzie and Roger's [1977] nontronite heated to 580°C, but their fit does not allow a comparison of only the *cis* sites.

No features seen in any of the heating experiments resemble the 180-kbar sample (Figure 4). This supports our hypothesis that the dominant effect was disordering among the octahedral sites associated with the shock event. The 300-kbar sample resembles the sample heated to 350°C both in isomer shift and in the asymmetry of the peak (compare Figures 5 and 6). In the 300-kbar sample the asymmetry is better developed, and the quadrupole splitting is wider. We

interpreted the 300-kbar sample as a mixture of tetrahedral and octahedral  $\text{Fe}^{3+}$  (though the alternative is a change in all of the  $\text{Fe}^{3+}$  sites toward a lower isomer shift, see Figure 5a). In the 350°C sample, following the analogy of Heller-Kallai and Rozenson [1980], we inferred a shift toward 5-fold coordination as the  $\text{OH}^-$  are stripped out of the octahedral layer of the clay. While the distinction between a mixture of 4- and 6-fold coordination and only 5-fold coordination is hard to resolve with our data, the asymmetry of the Mössbauer spectra, especially in the 300-kbar sample, and the fact that an unconstrained fit of the 300-kbar sample yields an isomer shift that matches tetrahedral  $\text{Fe}^{3+}$  is intriguing. This asymmetry would be difficult to detect in samples that initially contain tetrahedral or *trans* octahedral  $\text{Fe}^{3+}$  because the peaks due to those sites would mask any tetrahedral  $\text{Fe}^{3+}$  formed by heating. In either case, the coordination number of the  $\text{Fe}^{3+}$  in the nontronite has decreased in both the heated and impacted nontronite.

This decrease in coordination number can be explained if we consider the dehydroxylation of nontronite. Two  $\text{OH}^-$  anions must combine to produce  $\text{O}^{2-}$  and a water molecule that migrates out. The remaining  $\text{O}^{2-}$  satisfies the charge requirements. If both of the  $\text{OH}^-$  anions are adjacent to a  $\text{Fe}^{3+}$ , a 5-fold site would be produced. Depending on the strength of the structure and the number of  $\text{OH}^-$  stripped out of the octahedral layer, there would be a tendency to form a mixture of sites with 4- and 6-fold coordination. This would greatly distort the nontronite structure, which is observed in the increase of quadrupole splitting with increased dehydroxylation. Locally, where abundant structural water has been removed, the octahedral layer could resemble a maghemite structure.

If the change in the Riverside nontronite shocked to 300 kbar were due only to the shock heating, it would appear that the sample, on the average, was heated the equivalent of slightly higher than 350°C and considerably less than 500°C. However, since the shocked sample was heated and cooled much faster, a much greater shock temperature is probably necessary to produce the same effect. Since the 180-kbar sample shows only a slight color change and no measurable loss of  $\text{OH}^-$  water, it was not effectively heated above about 300°C, the temperature  $\text{OH}^-$  begins to leave the clay structure [MacKenzie and Rogers, 1977]. Also, the observation that the 180-kbar sample cannot be matched by heating suggests that shocking produces effects that are unique.

#### The Color Change

The color change is caused by a shift in the edge of the  $\text{O}^{2-}\text{-Fe}^{3+}$  charge transfer absorptions into the visible part of the spectrum. This can be caused by actually shifting the position of the absorption associated with the  $\text{Fe}^{3+}$  in the nontronite or by adding a new component that absorbs at a slightly higher wavelength; the resulting combination of components would be difficult to distinguish from an actual shift in the edge. While neither possibility can be eliminated, the first, that an actual shift occurred, is more consistent with the mineralogical changes.

The decrease in the coordination number of the  $\text{Fe}^{3+}$  could cause the change in the  $\text{O}^{2-}\text{-Fe}^{3+}$  charge transfer absorption edge. The presence of  $\text{Fe}^{3+}$  in tetrahedral coordination in minerals where  $\text{Fe}^{3+}$  is dominantly in octahedral coordination causes a similar color difference; for example, the difference between certain yellow and brown garnets is caused by a small amount of tetrahedrally coordinated  $\text{Fe}^{3+}$  in the latter [Manning, 1972; C. Solomon, unpublished paper, 1979]. One possible problem with this interpretation may be the presence of tetrahedral  $\text{Fe}^{3+}$  in many yellow nontronites [Goodman et al., 1976]. While only one other worker [Brunot, 1973] has reported tetrahedrally coordinated  $\text{Fe}^{3+}$  in nontronites, if Goodman et al. [1976] are correct, these pale yellow nontronites have almost as much tetrahedral  $\text{Fe}^{3+}$  as our reddish brown nontronite (see Table 1). The solution to this apparent contradiction probably relates to the location of 4-fold coordinated  $\text{Fe}^{3+}$ . In natural nontronites, a certain percentage of the tetrahedra in the silica layers are occupied by  $\text{Fe}^{3+}$  [Goodman et al., 1976]. As heating occurs, what started as the  $\text{Fe}^{3+}$  octahedral layer, which contains the structural water, changes; the tetrahedra, whether occupied by  $\text{Si}^{4+}$  or  $\text{Fe}^{3+}$ , apparently do not participate until much higher temperatures. Therefore, the structural configuration resulting from the observed coordination change with heating or shock loading is quite different from having a portion of the tetrahedral sites initially filled with  $\text{Fe}^{3+}$  instead of  $\text{Si}^{4+}$ .

A second possibility, that is consistent with all of the data but lacks positive evidence, is that upon heating or shock loading a portion of the Riverside nontronite decomposed, creating an iron oxide as a pigment. If this is the case, all of the changes noted above occur, but localized concentration of the effect breaks small parts of the nontronite into oxides, coloring the rest of the largely unchanged nontronite. Mixing experiments indicate that as little as 1% hematite or maghemite could cause the color change observed if the samples are thoroughly mixed. This would be below the detection limit of X-ray, IR, and Mössbauer spectroscopy. In an effort to test this possibility a sample of Riverside nontronite shocked to 300 kbar was examined with a cryogenic magnetometer to detect magnetic oxides. The only magnetic material detected was metallic (recognized by the low coercivity), probably from the sample holder. While the metal could have masked some other magnetic material, it was considered very unlikely that candidate red minerals, like hematite or maghemite, could have been present in sufficient quantities to color the sample (D. Van Alstine, personal communication, 1980). Also, the spectral change would require an oxide with a featureless absorption pattern in the optical and near-IR region.

MacKenzie and Rogers [1977, p. 183] report that maghemite starts to appear in ferric nontronites heated above 300°C in air. While we could not detect any maghemite with the same techniques, their observation could be used to infer that the nontronite begins to break down locally long before it completely dissociates at temperatures greater than 600°C. However, several of their starting nontronite samples have a six-line

component in their Mössbauer spectra that is probably goethite or lepidocrosite [see MacKenzie and Rogers, 1977, Figures 5-7]. This six-line component converts at about 300°C to a six-line spectra corresponding to maghemite. While it is possible that maghemite is also produced from the nontronite (as MacKenzie and Rogers, [1977] seem to suggest), we feel that the most likely source of the maghemite is a contaminating hydroxide, not the clay itself.

As a variation on this last possibility, our Riverside nontronite could have included a small undetectable amount of iron hydroxide (goethite or lepidocrosite, for example) that dehydrated to produce a red iron oxide pigment. This explanation of the data suffers from the problem of not being consistent with the continuous nature of the color change with increased heating far above the temperature necessary to dehydrate the hydroxides [Deer et al., 1966]. Also, the appropriate oxide would have to have an optical spectra almost exactly like Riverside nontronite.

Color changes in iron-bearing minerals are commonly due to changes in the oxidation state of the iron. This is not a possibility for Riverside nontronite for two reasons. First, Riverside nontronite had no detectable  $\text{Fe}^{2+}$  either before or after impact. Second, nontronites subjected to oxidation-reduction experiments range in color from yellow to green or blue green [Russell et al., 1979]. This range is well explained by the presence or absence of the  $\text{Fe}^{2+}$  crystal field absorptions near 1000 nm. The only possibility would be that the presence of less than 1%  $\text{Fe}^{2+}$  could substantially affect the position of the  $\text{O}^{2-}\text{-Fe}^{3+}$  absorption. If this were the case, redox experiments should produce reddish brown nontronites, and they do not.

#### Other Examples

There are several other examples where spectral changes were observed in impact experiments. Rhodonite ( $\text{MnSiO}_3$ ) undergoes a color change from pink to colorless, due to the shock-induced reduction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  [Gibbons et al., 1974]. Adams et al., [1979] found that plagioclase and, to a lesser degree, enstatite changed spectrally with increasing shock loading. They attribute the changes in plagioclase to the production of maskelynite and, eventually, glass. Several workers have reported pressure-induced, reversible reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in a variety of minerals [e.g., Drickamer et al., 1970; Burns et al., 1972]. Our experiment, however, provides a new mechanism that does not require an oxidation-reduction reaction involving the cation or the melting of the mineral.

#### The Color of the Martian Fines

There are several questions that must be addressed in applying our findings to Mars. First of all, is there nontronite, or anything like it, on Mars? Second, can sufficient quantities of reddened nontronite be produced on Mars? Third, is there any reason to appeal to such an exotic process to color Mars? From a chemical and mineralogical point of view, nontronite is an attractive candidate mineral for a significant portion of the Martian fines [Toulmin et al.,



1977]. Mechanisms known to be operating on Mars, impactation, volcanism, and erosion commonly produce clays in the presence of water. Spectral studies, indicating the presence of iron in the ferric state and smectitelike silicates, are consistent with nontronite or similar clays [Hunt et al., 1973; Toon et al., 1977; Singer et al., 1979].

While it is difficult to compare our absorption spectra (Figure 1) with reflectance data, the general features of Riverside nontronite are quite like the Martian bright regions (Figure 8a, reproduced from Singer et al. [1979]). There is a steep drop in absorption (increase in reflectance) from the near-UV into the visible and a very featureless near-IR region. The major difference is the lack of an absorption minimum (reflectance maximum) near  $0.75\ \mu\text{m}$  and the corresponding (?) absorption maximum (reflectance minimum) near  $0.87\ \mu\text{m}$ . Features like these are characteristic of iron oxides [e.g., Singer, 1981b; Sherman et al., 1981], which we know from the magnetic experiments must form a portion of the Martian fines [Hargraves et al., 1977]. The exact position of the absorption edge in Riverside nontronite depends on the hydroxylation of the  $\text{Fe}^{3+}$  cation, as discussed above, and strong variations in color result from shifts in this edge.

At the Viking lander sites, fine material varies in color from moderate to dark yellowish brown (10YR-2Y) 3-4/3-4 [Huck et al., 1977]. Riverside nontronite started less red and somewhat brighter, 2.5 Y 6/6, than any of the Martian

surface material, and after being shocked to 300 kbar it became both redder and darker, 7.5 YR 4/6, than the Martian fines. So the variation in color seen at the lander sites is bracketed by the variation in color of shocked Riverside nontronite. The chroma or color saturation (both shocked and unshocked) of Riverside nontronite is greater than that of the Martian surface material (6 versus 3-4). This may suggest the presence of some less strongly colored material mixed with nontronite. However, Riverside nontronite is more strongly colored than many nontronites, so the difference in chroma need not be significant.

Recently, Singer [1981a] has presented evidence suggesting that nontronite cannot be a major constituent of the Martian fines. He also presents similar evidence limiting the amount of various ferric oxides in the Martian fines [Singer, 1981b]. While we agree with his ultimate conclusion, that a good match for the Martian fines is a palagonite or some similar fine-grained or amorphous alteration product of mafic rock or glass, we feel that the elimination of nontronite (along with other clays) and crystalline iron oxides as major components of the Martian fines is not conclusively demonstrated by his experiments. Since other workers have also abandoned the clay-rich model for the Martian fines [e.g., Allen et al., 1981; Evans et al., 1981; McCord et al., 1981], we feel that it is important to elaborate on the spectral properties of nontronite.

Once it was realized that certain nontronites resembled the chemistry of the Martian fines, the Viking XRF Team studied many nontronites in an attempt to match the Viking fluorescence spectra with a natural sample [Baird et al., 1977, personal communication, 1981]. One of the samples considered was Pennsylvania nontronite (Wards Nat. Sci. Est.). Like most of the pure, greenish ferroan nontronites studied by the Viking XRF Team, it was a poor match for the fluorescence data (A. K. Baird, personal communication, 1981). Also, because of its green color, it seemed particularly unlikely as a candidate mineral for the red planet. Singer (see Figure 8b, reproduced from Singer [1981a]) also found that this sample provided a poor match for the Martian optical and near-IR spectra. Green nontronites exhibit strong crystal field absorptions due to  $\text{Fe}^{2+}$  in the visible to near IR. This absorption is probably the  $0.95\text{-}\mu\text{m}$  feature in the spectrum reported by Singer, inasmuch as he removed the iron oxide contaminants that could absorb there [Singer, 1981a]. Reduction studies of nontronites show that a pale yellow nontronite will turn emerald green to blue green when about 10% of its ferric iron is reduced to ferrous iron [Russell et al., 1979, p. 64]. A natural ferroan nontronite with about 10% of its iron in the ferrous state is dark olive green [MacKenzie and Rogers, 1977]. Colors between pale yellow and green (or even blue green) represent  $\text{Fe}^{2+}$  contents less than 10%. We would predict, from its color, that the Pennsylvania nontronite probably has only several percent  $\text{Fe}^{2+}$ . Riverside nontronite, shown by Weldon et al. [1980, Figure 1, p. 1235] and Figure 1, this paper, does not have a resolvable  $\text{Fe}^{2+}$  absorption. As noted in the discussion of the optical spectra, this is consistent with published spectra of ferric nontronite [Karickhoff and Bailey, 1973] and is in contrast to the ferroan Pennsylvania

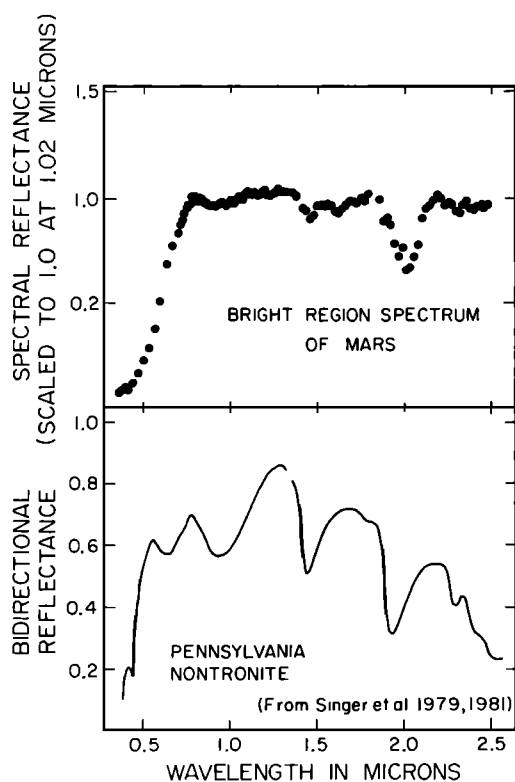


Fig. 8. Reflectance spectra of the bright region of Mars and Pennsylvania nontronite. Reflectance spectra can crudely be compared with absorbance spectra by inversion of the vertical scale. See text for the discussion of the comparison with Figure 1.

nontronite. Clearly, green, ferroan nontronites like the Pennsylvanian nontronite are unlikely candidates for the Martian fines. However, this does not suggest that ferric nontronites, like Riverside nontronites, are not good matches for the spectral properties of Mars.

In the spectra presented by Singer [1981a, b], the absorptions due to the various crystal field transitions in both the nontronite and montmorillonite are quite sharp and well defined, as are the absorption bands in the spectra of iron oxides and mixtures containing iron oxides. This is in contrast to the spectra of Mars and spectra of palagonites and similar alteration products of mafic rocks and glass. For this reason, Singer prefers an 'amorphous' siting for the  $\text{Fe}^{3+}$  on Mars. While this may be the case, we suspect that his palagonites and other 'amorphous gels' have significant amounts of nontronite and iron oxides which are the usual end-members of palagonitization and alteration of iron-rich mafic glasses [Deer et al., 1966; Toulmin et al., 1977; Walker and Blake, 1966]. The Riverside nontronite sample exhibits very diffuse bands like Singer's 'gels' but is certainly dominantly nontronite. It is probably not nearly as homogeneous or uniform as the Pennsylvania nontronite. Since clays and other weathering products are extremely variable we feel that more study should be done to help characterize the Martian spectra.

If the impact-coloring mechanism acting on nontronite were important on Mars, we would expect that such a process should operate efficiently where the presence of deposits of fines are abundant enough to provide targets that would produce significant amounts of shocked nontronite. Such deposits may be available in the layered and the undulating terranes of the north polar region. It has been proposed that these deposits are being formed by the precipitation of  $\text{CO}_2$  ice, scavenging and retaining dust from the atmosphere at the pole [Pollack et al., 1979; Cutts et al., 1979]. If this is the case, they should provide ideal targets for producing large quantities of shocked nontronite.

Since it appears that there are appropriate targets available on Mars, we have crudely calculated the amount of reddened material that is likely to be produced from a cratering event and what long-term production is likely from the estimates of cratering rates on Mars. We considered crater sizes between 0.1 and 20 km (for which good statistics exist) and used a pressure cutoff of 200 kbar for a discernable color change. The near-field pressure decay function of distance from the center point of impact was taken from Kieffer and Simonds [1980], which is a modification of that of Gault and Heitowitz [1963]. The relation between crater diameter and impact energy came from high explosion cratering data [Oberbeck, 1977].

We found that approximately  $10^{-4}$  or 0.01% of the material excavated in a cratering event on Mars would show a discernable color shift toward red if the target were made of Riverside nontronite. While this may seem a small number, this highly shocked material is ejected at the highest velocities and angles and would end up on the surface of the planet [Ahrens and O'Keefe, 1978]. We suggest that the ejecta blankets around craters into fine Martian deposits could be

discernably redder and darker than the surrounding material. Also, this mechanism preferentially injects the reddest material into the atmosphere and onto the surface where it is available for reworking and concentration. To calculate the long-term production, we used the recent production function of craters between 0.1 and 20 km [Neukum et al., 1975] with our conservative estimate of the amount of material shocked above 200 kbar (0.01%). We used a constant mean impact velocity for meteorites at Mars [Hartmann, 1977]. Using these values, we determined that about 10 cm/b.y. averaged over the surface of Mars is being produced by cratering. Since we used minimum values in our calculations and only considered craters between 0.1 and 20 km, a greater rate is probably more reasonable. Also, since the current crater production rate is probably lower than at any time in the past [Neukum and Hiller, 1981], the production rate of shocked nontronite would have been much higher in the past. However, this rate is low enough that it appears that impact-induced color changes are probably more effective at changing the distribution and variation in color rather than greatly affecting the overall color of Mars.

Finally, we come to the question of the necessity of applying this to Mars. The processes that produce the weathering products that form the Martian fines are probably sufficient to give the red planet its characteristic color. The oxidation of the  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  certainly could provide oxides to color Mars far redder than it is while forming clays and other minerals. However, mixing experiments indicate that only a small fraction of the iron on Mars can be in strongly colored oxides like hematite or maghemite. Since the chemistry and color of the Martian fines require silicates like nontronite to hold most of the  $\text{Fe}^{3+}$ , a mechanism that colors Mars with clay impacted to various degrees may make the presence of such oxides unnecessary. Magnetite could be the appropriate magnetic and opaque oxide [e.g., Pollack et al., 1977] not maghemite, as suggested by Hargraves et al. [1977]. So, while there is already an abundance of mechanisms to color Mars, the present impact-coloring mechanism allows for the possibility of a Mars essentially free of such minerals like goethite, hematite, and maghemite. Also, it provides a process that could explain spectral variations that are spatially different and relate to impact history rather than weathering on Mars. For example, it has long been known that Mars is essentially bimodal in spectral distribution: bright red and dark nonred. Bright red areas generally correspond with dust or fines, and dark nonred areas typically have large amounts of exposed rock; most areas can be explained by a mixture of both [Singer et al., 1979]. In some cases, however, dark areas are also red [Soderblom et al., 1977]. In fact, some of the oldest and most intensely impacted terranes are among the reddest [Soderblom et al., 1978].

### Conclusions

Shock recovery experiments carried out on Riverside nontronite caused a marked color change in the clay from olive-yellow to strong brown upon recovery from shock loading to peak pressures of 180 to 300 kbar. The color change spans the color

range observed in the fine material at the Viking lander sites. The change in color is attributed to a shift in the  $O^{2-}-Fe^{3+}$  charge transfer bands to longer wavelengths, causing the material to become both redder and darker. The observations that the color change is associated with the dehydroxylation of the clay and Mössbauer spectra that show a lowering of the coordination number of the  $Fe^{3+}$  as the  $OH^-$  is removed from the structure suggest that the movement of the absorption bands into the visible is caused by the formation of 4-fold or distorted 5-fold-like  $Fe^{3+}$  within the octahedral layers of the clay. While this process is similar to thermal decomposition of nontronite, there are some indications that the result of shock heating may be somewhat different from simple heating of the clay.

Despite recent suggestions [Singer, 1981a], ferric nontronite appears to be both spectrally and chemically a good candidate for a major component of the Martian fines. Since deposits thick enough to provide targets for cratering events appear to exist in the polar layered and mantled terranes some component of the color of Mars could be due to impactation. Using a threshold of 200 kbar for a discernable color change, we calculate that about  $10^{-4}$  of the material excavated by an impact into Martian surface material would be significantly reddened and darkened if it were dominantly nontronite. At current cratering rates it seems unlikely that impactation is affecting the absolute color of Mars to any great degree, but variations in color between heavily impacted terranes and color distributions associated with individual craters may be influenced by this process.

**Acknowledgments.** We appreciate the experimental assistance of J. Long, E. Gelle, and M. Long in the shock experiments. We thank A. Baird for samples of nontronite and helpful discussion. We are indebted to G. Rossman, R. Aines, and S. Mattson for assistance in optical and IR sample analysis and interpretation. S. Rigden aided in X-ray diffraction preparation. We thank E. Stolper and D. Van Alstine for performing the heating and magnetometer experiments. M. Lange provided informative discussions regarding cratering calculations. S. Yamada typed the final manuscript. We appreciate the efforts of the reviewers. This research was supported by NASA (NGL-05-002-105), contribution 3726, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

#### References

- Adams, J. B., F. Hörz, and R. V. Gibbons, Effects of shock loading on the reflectance spectra of plagioclase, pyroxene and glass (abstract), *Lunar Planet. Sci.*, **X**, 1-3, 1979.
- Ahrens, T. J., and J. D. O'Keefe, Energy and mass distributions of impact ejecta blankets on the Moon and Mercury, *Proc. Lunar Planet. Sci. Conf.*, 9th, 3787-3802, 1978.
- Allen, C. C., J. L. Gooding, M. J. Jericnovic, and K. Keil, The surface soil of Mars, paper presented at the Third International Colloquium on Mars, NASA, Pasadena, California, 1981.
- Armstrong, R. J., A. H. Morrish, and G. A. Sawatzky, Mössbauer study of ferric ions in the tetrahedral and octahedral sites of a spinel, *Phys. Lett.*, **23**, 414-416, 1966.
- Baird, A. K., A. J. Castro, B. C. Clark, P. Toulmin III, H. J. Rose, Jr., K. Keil, and J. L. Gooding, Viking X-ray fluorescence experiment: Sampling strategies and laboratory simulations, *J. Geophys. Res.*, **82**, 4595-4624, 1977.
- Bancroft, G. M., *Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists*, John Wiley, New York, 1973.
- Berkowitz, A. E., W. J. Schuele, and P. J. Flanders, Influence of crystallite size on the magnetic properties of acicular  $\gamma-Fe_2O_3$  particles, *J. Appl. Phys.*, **39**, 1261-1262, 1968.
- Berry, L. G. (Ed.), *Selected Powder Diffraction Data for Minerals*, Joint Committee on Powder Diffraction Standards, Swarthmore, Pa., 1974.
- Boslough, M. B., R. J. Weldon, and T. J. Ahrens, Impact-induced water loss from serpentine, nontronite and kernite, *Proc. Lunar Planet. Sci. Conf.*, 11th, 2145-2158, 1980.
- Brunot, B., Application of the Mössbauer effect to the study of clay minerals: A hydrothermal nontronite and a nontronite from Lake Malawi, *Neues Jahrb. Mineral. Monatsh.*, 452-461, 1973.
- Burns, R. G., J. A. Tossell, and D. J. Vaughan, Pressure-induced reduction of a ferric amphibole, *Nature*, **240**, 33-35, 1972.
- Clark, B. C., A. K. Baird, H. J. Rose, P. Toulmin, K. Kiel, A. J. Castro, W. C. Kelliher, C. D. Rowe, and P. H. Evans, Inorganic analyses of Martian surface samples at the Viking landing sites, *Science*, **194**, 1283-1288, 1976.
- Clark, B. C., III, A. K. Baird, H. J. Rose, Jr., P. Toulmin III, R. P. Christian, W. C. Kelliher, A. J. Castro, C. D. Rowe, K. Keil, and G. R. Huss, Viking X-ray fluorescence experiment: Analytical methods and early results, *J. Geophys. Res.*, **82**, 4577-4594, 1977.
- Clark, B. C., A. K. Baird, R. J. Weldon, D. M. Tsusaki, L. Schnabel, and M. P. Candelaria, Chemical composition of Martian fines, *J. Geophys. Res.*, this issue.
- Coey, J. M. D., Noncollinear spin arrangement in ultrafine ferrimagnetic crystallites, *Phys. Rev. Lett.*, **27**, 1140-1142, 1971.
- Cutts, J. A., K. R. Blausius, and W. J. Roberts, Evolution of Martian polar landscapes: Interplay of long-term variations in perennial ice cover and dust storm intensity, *J. Geophys. Res.*, **84**, 2975-2994, 1979.
- Deer, W. A., R. A. Howie, and J. Zussman, *An Introduction to the Rock Forming Minerals*, Longman, London, 1966.
- Drickamer, H. G., V. C. Bastron, D. C. Fisher, and D. C. Grenoble, The high pressure chemistry of iron, *J. Solid State Chem.*, **2**, 94-104, 1970.
- Evans, D. L., J. B. Adams, T. G. Farr, T. L. Roush, and R. B. Singer, Terrestrial and synthetic analogs to Martian weathering products, paper presented at the Third International Colloquium on Mars, NASA, Pasadena, Calif., 1981.
- Gault, D. E., and E. D. Heitowit, The partition

- of energy for hypervelocity impact craters formed in rock, in Proceedings of the 6th Hypervelocity Impact Symposium, pp. 420-456, Cleveland, Ohio, 1963.
- Gibbons, R. V., T. J. Ahrens, and G. R. Rossman, A spectrographic interpretation of the shock-produced color change in Rhodonite ( $\text{MnSiO}_3$ ): The shock-induced reduction of  $\text{Mn(III)}$  to  $\text{Mn(II)}$ , Am. Mineral., **59**, 177-182, 1974.
- Goodman, B. A., The Mössbauer spectra of nontronites: Consideration of an alternative assignment, Clays Clay Miner., **26**, 176-177, 1978.
- Goodman, B. A., J. D. Russell, and A. R. Fraser, A Mössbauer and IR spectroscopic study of the structure of nontronite, Clays Clay Miner., **24**, 53-59, 1976.
- Greenwood, N. N., and T. C. Gibb, Mössbauer Spectroscopy, Chapman and Hall, London, 1971.
- Hargraves, R. B., D. W. Collinson, R. E. Arvidson, and C. R. Spitzer, The Viking magnetic properties experiment: Primary mission results, J. Geophys. Res., **82**, 4547-4558, 1977.
- Hartmann, W. K., Relative crater production rates on planets, Icarus, **31**, 260-276, 1977.
- Heller-Kallai, L., and I. Rozenson, Dehydroxylation of dioctahedral phyllosilicates, Clays Clay Miner., **28**, 355-368, 1980.
- Huck, F. O., D. J. Jobson, S. K. Park, S. D. Wall, R. E. Arvidson, W. R. Patterson, and W. D. Benton, Spectrophotometric and color estimates of the Viking lander sites, J. Geophys. Res., **82**, 4401-4411, 1977.
- Hunt, G. R., L. M. Logan, and J. W. Salisbury, Mars: Components of infrared spectra and the composition of the dust cloud, Icarus, **18**, 459-469, 1973.
- Karickhoff, S. W., and G. W. Bailey, Optical absorption spectra of clay minerals, Clay Clay Miner., **21**, 59-70, 1973.
- Kieffer, S. W., and C. H. Simonds, The role of volatiles and lithology in the impact cratering process, Rev. Geophys. Space Phys., **18**, 143-181, 1980.
- MacKenzie, K. J. B., and D. E. Rogers, Thermal and Mössbauer studies of iron-containing hydrous silicates, I, Nontronite, Thermochim. Acta, **18**, 177-196, 1977.
- Manning, P. G., Optical absorption spectra of  $\text{Fe}^{3+}$  in octahedral and tetrahedral sites in natural garnets, Can. Mineral., **11**, 826-839, 1972.
- McCord, T. B., R. B. Singer, B. R. Hawke, J. B. Adams, D. L. Evans, J. W. Head, P. J. Monginis-Mark, C. M. Pieters, R. L. Huguenin, and S. H. Zisk, Mars: Definition and characterization of global surface units, with compositional emphasis, paper presented at the Third International Colloquium on Mars, NASA, Pasadena, Calif., 1981.
- Mering, T., and A. Oberlin, Electron-optical study of smectites, Clays Clay Miner., **15**, 3-25, 1967.
- Munsell, J. T., Soil color charts, Munsell Color: MacBeth Div., Kollmorgen Corp., Baltimore, Md., 1975.
- Neukum, G., and K. Hiller, Martian ages, J. Geophys. Res., **86**, 3097-3121, 1981.
- Neukum, G., B. König, H. Fechtig, and D. Storzer, Cratering in the earth-moon system: Consequences for age determination by crater counting, Proc. Lunar Sci. Conf., **5th**, 2597-2620, 1975.
- Oberbeck, V. R., Application of high explosion cratering data to planetary problems, in Impact and Explosion Cratering, edited by D. J. Roddy, R. O. Pepin, and R. B. Merrill, pp. 45-66, Pergamon, New York, 1977.
- Pollack, J. B., D. Colburn, R. Kahn, J. Hunter, W. Van Camp, C. E. Carlston, and M. R. Wolf, Properties of aerosols in the Martian atmosphere as inferred from Viking lander imaging data, J. Geophys. Res., **82**, 4479-4496, 1977.
- Pollack, J. B., D. S. Colburn, F. M. Flasar, R. Kahn, C. E. Carlston, and D. Pidek, Properties and effects of dust particles suspended in the Martian atmosphere, J. Geophys. Res., **84**, 2929-2945, 1979.
- Rozenson, I., and L. Heller-Kallai, Mössbauer spectra of dioctahedral smectites, Clays Clay Miner., **25**, 94-101, 1977.
- Russell, J. D., and D. R. Clark, The effect of Fe for Si substitution on the b-dimension of nontronite, Clay Miner., **13**, 133-136, 1978.
- Russell, J. D., B. A. Goodman, and A. R. Fraser, Infrared and Mössbauer studies of reduced nontronites, Clays Clay Miner., **27**, 63-71, 1979.
- Sherman, D. M., V. M. Burns, and R. G. Burns, Diffuse reflectance spectra of the iron oxides and their application to the Martian bright region mineralogy, paper presented at the Third International Colloquium on Mars, NASA, Pasadena, Calif., 1981.
- Singer, R. B., Spectral constraints on iron-rich smectites as abundant constituents of Martian soils, Lunar Planet. Sci., **XII**, 996-998, 1981a.
- Singer, R. B., Some observational constraints on iron mineralogy in Martian bright soils, paper presented at the Third International Colloquium on Mars, NASA, Pasadena, Calif., 1981b.
- Singer, R. B., T. B. McCord, and R. N. Clark, Mars surface composition from reflectance spectroscopy: A summary, J. Geophys. Res., **84**, 8415-8426, 1979.
- Soderblom, L. A., K. Edwards, E. M. Eliason, E. M. Sanchez, and M. P. Charette, Global color variations on the Martian surface, Icarus, **34**, 446-464, 1978.
- Sprenkel-Segel, E. L., Recoilless resonance spectroscopy of meteoritic iron oxides, J. Geophys. Res., **75**, 6618-6630, 1970.
- Taylor, G. L., A. P. Ruotsala, and R. O. Keeling, Jr., Analysis of iron in layer silicates by Mössbauer spectroscopy, Clays Clay Miner., **16**, 381-391, 1968.
- Toon, O. B., J. B. Pollack, and C. Sagan, Physical properties of the particles composing the Martian dust storm of 1971-1972, Icarus, **30**, 663-696, 1977.
- Toulmin, P., III, A. K. Baird, B. C. Clark, K. Keil, H. J. Rose, P. H. Evans, and W. C. Kelliher, Geochemical and mineralogic interpretation of the Viking inorganic chemical results, J. Geophys. Res., **82**, 4625-4634, 1977.

Walker, G. P. L., and D. H. Blake, The formation of a palagonite breccia mass beneath a valley glacier in Iceland, Q. J. Geol. Soc. London, 122, 45-61, 1966.

Weldon, R. J., M. B. Boslough, and T. J. Ahrens, Shock-induced color changes in

nontronite: A possible Martian surface process, Lunar Planet. Sci. Conf., XI, 1234-1235, 1980.

(Received December 15, 1981;

revised April 27, 1982;

accepted June 18, 1982.)